

THE REACTION OF CYCLOPENTADIENYLIDINE, FLUORENYLIDENE AND TETRACHLOROCYCLOPENTADIENYLIDENE WITH ALCOHOLS. A LASER FLASH PHOTOLYSIS STUDY

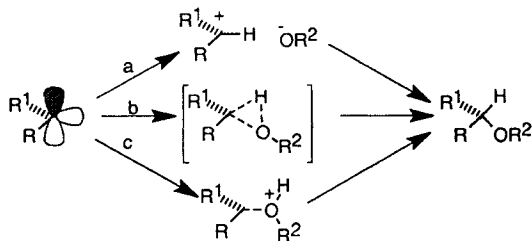
DAVID R. OLSON AND MATTHEW S. PLATZ*

Department of Chemistry, Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210, USA

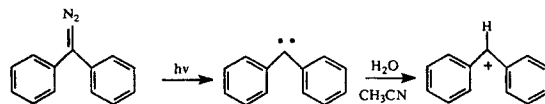
Rate constants of reaction of cyclopentadienylidene, fluorenylidene and tetrachlorocyclopentadienylidene with alcohols and other quenchers were determined by laser flash photolysis methods. The rate constants of reaction of cyclopentadienylidene and fluorenylidene with various alcohols were determined and found to increase with increasing alcohol acidity. Alcohols as a group reacted faster with cyclopentadienylidene and fluorenylidene than likely ylide formers such as pyridine, ethyl acetate and tetrahydrofuran. Brønsted plots of the reaction of cyclopentadienylidene and fluorenylidene with alcohols are linear with slopes of 0.061 and 0.082, respectively. In the case of tetrachlorocyclopentadienylidene, an ylide type of reaction mechanism with alcohols is indicated. Tetrachlorocyclopentadienylidene reacts most rapidly with the least acidic alcohol studied and this carbene reacts more rapidly with tetramethylurea, pyridine and tetrahydrofuran than with methanol.

INTRODUCTION

Singlet carbenes can react with substrates by a number of conceivable mechanistic pathways because of their zwitterionic nature. Alcohols also have the ability to react as either a Lewis acid or base. Previous studies of the reactions between alcohols and carbenes have been eloquently discussed by Kirmse¹ in a recent review. The ambiphilic nature of both alcohols and carbenes is reflected in three possible reaction mechanisms that are commonly considered for this formal insertion reaction: (a) protonation of the carbene followed by nucleophilic attack on the resulting carbocation, (b) concerted insertion into the O–H bond or (c) ylide formation between the carbene and alcohol and subsequent proton transfer. The preferred mechanistic pathway is expected to depend on the exact nature of R, R¹ and R².



Laser flash photolysis (LFP) methods have been used to directly detect carbene intermediates and to measure the rates of reaction of these species with different alcohols.² Reaction rates have been determined by directly monitoring the quenching of triplet carbene transient absorption or by competition for the carbene between the alcohol and an ylide-forming reagent such as pyridine or acetonitrile. In the case of diphenylcarbene (DPC), and several of its substituted derivatives, the protonation mechanism has been established by the direct detection of benzhydryl cation resulting from the reaction of water with DPC generated by LFP methods.³



Unlike cations, the initially formed ylide intermediates of pathway (c) have not been detected directly.^{1,2} With the exception of (alkoxycarbonyl)carbenes,^{1,4} evidence for ylide formation in large part results from differences in the products formed from the carbene and the authentic cation.⁵

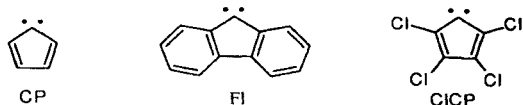
* Author for correspondence.

In addition to the carbenes which appear to react via the cationic or ylide mechanistic categories, some hydroxyalkyl-substituted arylcarbenes appear to react by a combination of both of these mechanisms.⁶

Much of the interest in cyclopentadienylidene (CP) has centered on how contributions from aromatic structure 1 may be reflected in its reactivity.

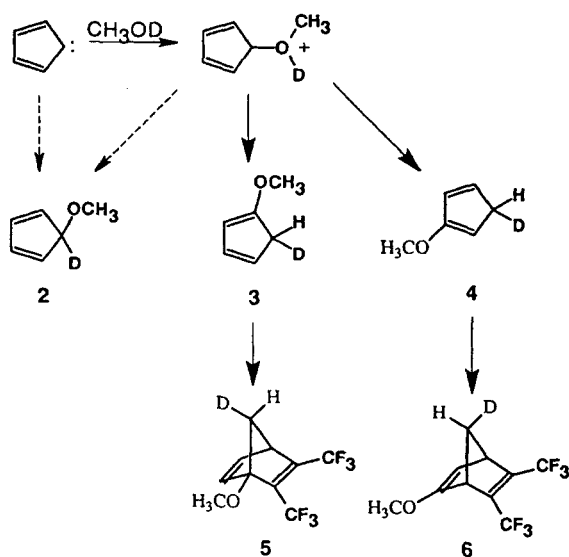


Because of structure 1, the carbenes CP, fluorenylidene (Fl) and tetrachlorocyclopentadienylidene (ClCP) may be expected to react with alcohols by pathway (c) as a result of their electrophilicity, the aromaticity of the anticipated ylide intermediate and a desire to avoid the formation of an anti-aromatic cyclopentadienyl cation-like structure produced in a proton transfer reaction.



CP, ClCP and especially Fl have all been studied previously in some detail. The predominantly singlet reactivity pattern of CP has been demonstrated by its highly stereospecific (95%) addition to alkenes,⁷ while attempts to observe triplet CP chemistry by using octafluorocyclobutane as an inert diluent have failed.⁸ Generation of CP in 4-methyl-*cis*-2-pentene at 77 K also resulted in stereospecific addition to the alkene, although triplet CP has been observed in a fluorocarbon matrix at 77 K.⁹ Singlet reactivity patterns predominate in spite of the fact that the triplet carbene is the ground state, as shown by calculations¹⁰ and low-temperature EPR studies.⁹ A preponderance of singlet chemistry from triplet ground-state carbenes is not unusual and occurs for many carbenes,¹ including Fl and ClCP, which have been shown to equilibrate between singlet and triplet states at room temperature.¹¹⁻¹⁴ However, unlike CP, ClCP exhibits a moderate degree of triplet reactivity in solution, as demonstrated by trapping studies with *cis*-alkenes. There is a significant yield of non-stereospecific addition products when ClCP reacts with alkenes.¹¹

In contrast to CP and ClCP, Fl has been extensively studied by LFP techniques.¹²⁻¹³ Fl has also been found to be a ground state triplet species. However, most of the chemistry observed from this carbene results from the more reactive singlet state which is in rapid equilibrium with the triplet carbene. Both the triplet carbene and the carbonyl *O*-oxide¹⁴ can be observed by LFP. The carbonyl *O*-oxide is either an ylide or singlet biradical-type structure produced by trapping of the triplet carbene by molecular oxygen.



Scheme 1

Trapping experiments performed by Kirmse *et al.*¹⁵ support an ylide mechanism for the reaction between cyclopentadienylidene and methanol in neat methanol. Photolysis of diazocyclopentadiene in methanol-OD and subsequent treatment with hexafluorobut-2-yne at -70°C resulted in a 4:1 mixture of 5 and 6 (Scheme 1). The absence of a trapping product resulting from 2 argues against a direct OD insertion process under these conditions, while the exclusive incorporation of deuterium at the 7-position of the norbornadiene product indicates that no more than one 1,5 D(H) shift transpired prior to Diels-Alder trapping of the diene.

Product studies of fluorenylidene by Kirmse *et al.*^{5a} indicated that there was relatively little difference between the reactivity of oxetane and methanol with this carbene. This result differed from the data obtained with diphenylcarbene, which reacts by the protonation mechanism. In this case methanol was found to be much more reactive than oxetane. This difference in the behavior of Fl from carbenes which react by the protonation pathway was taken as evidence that fluorenylidene reacts with methanol by ylide formation.

RESULTS

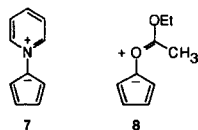
We studied CP, Fl and ClCP by LFP techniques and rate constants for the reaction of carbenes resulting from photolysis of diazocyclopentadiene, diazofluorene and tetrachlorodiazocyclopentadiene with various quenchers, including alcohols, were measured in an attempt to gain further mechanistic insight into these reactions. Rate constants were obtained by Stern-Volmer quenching of the formation of UV-visible detectable ylides

derived from the carbene and pyridine, acetonitrile or ethyl acetate. In general, the rate constants so obtained are considered to have a precision of $\pm 10\%$, although relative rate constants are likely to have significantly greater accuracy than the absolute values.

Cyclopentadienylidene

LFP (XeCl excimer, 308 nm) of diazocyclopentadiene (DCP) in 1,1,2-trichlorotrifluoroethane (Freon 113) fails to give a transient spectrum in the UV-visible region. Furthermore, no transient spectrum in the UV-visible region is observed when oxygen is bubbled through the solution for 2–3 min prior to irradiation. This differs from matrix studies where cyclopentadienone *O*-oxide has been detected by UV-visible¹⁶ ($\lambda_{\text{max}} = 420$ nm) and IR spectroscopy.¹⁷ However, this agrees with previous observations which indicate that although cyclopentadienylidene has a ground state triplet,^{9,10} little or no triplet reactivity is observed in fluid solution at ambient temperature and singlet reactivity predominates.^{7,8}

LFP of DCP in Freon 113 containing pyridine or in neat ethyl acetate (EA) produces transient spectra attributed to ylides **7** (Figure 1) and **8** (Figure 2), respectively.



The ylides are formed faster than the time resolution of our LFP system (< 20 ns), even at dilute concentrations (0.01 M) of ylide-forming reagent. The yield of ylide (A_y) varies sensibly with pyridine concentration. When the concentration of pyridine is small, A_y is small and increases to a maximum (A_y^∞) at 2.5 M pyridine (Figure 3). A plot of $1/A_y$

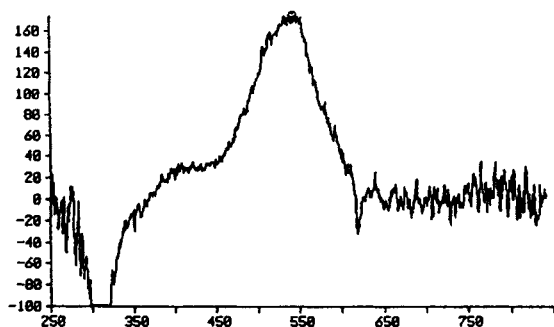


Figure 1. Transient absorption spectrum of **7** produced by LFP of diazocyclopentadiene in the presence of pyridine with Freon 113 as the solvent. The spectrum was recorded 500 ns after a 308 nm laser pulse over a window of 500 ns

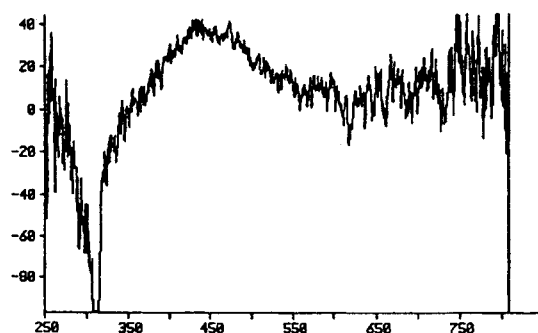


Figure 2. Transient absorption spectrum of **8** produced by LFP of diazocyclopentadiene in ethyl acetate. The spectrum was recorded 500 ns after a 308 nm laser pulse over a window of 500 ns

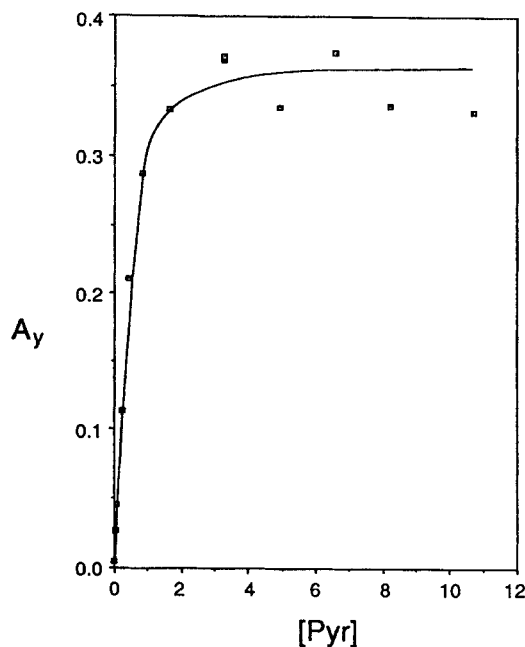


Figure 3. Plot of the yield (A_y) of the ylide **7** vs pyridine concentration for the reaction of cyclopentadienylidene with pyridine

versus $1/[\text{pyridine}]$ at low pyridine concentrations is linear (Figure 4). Division of the intercept by the slope of this plot yields $k_{\text{pyr}}K/(k_{\text{RX}}^1[\text{RX}]K + k_{\text{RX}}^3[\text{RX}]) = k_{\text{pyr}}\tau$, where the rate constants are as defined in Scheme 2¹⁸ and K is the singlet-triplet equilibrium constant. If ^1CP does not have time to relax to ^3CP in Freon 113 or if the spin-equilibrated carbene reacts only through its singlet state, the expression reduces to $k_{\text{pyr}}/k_{\text{RX}}[\text{RX}] = k_{\text{pyr}}\tau$, where τ is the lifetime of the singlet carbene (no spin relaxation) or of the spin-

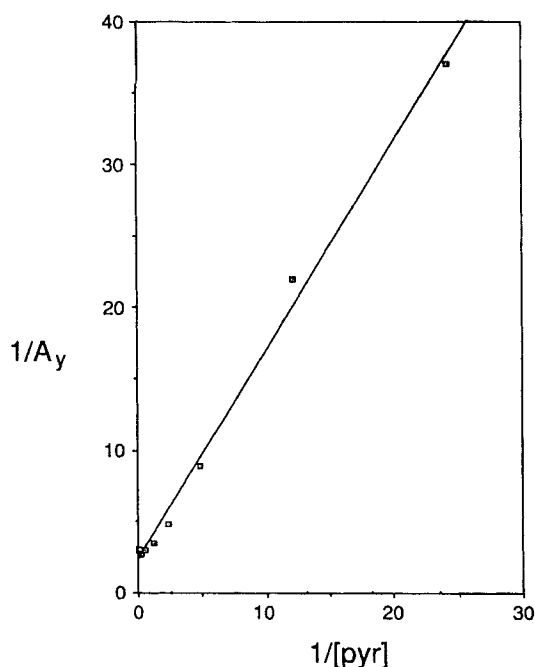
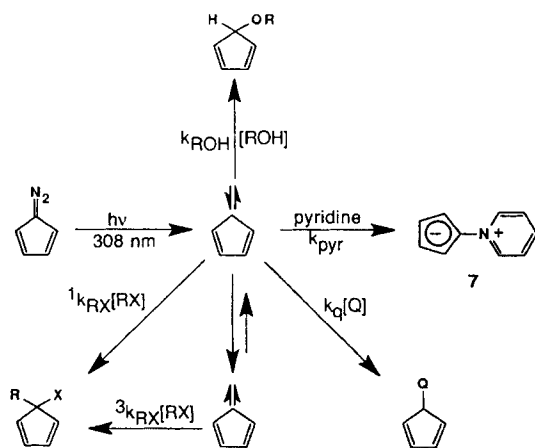


Figure 4. Double reciprocal plot for ylide 7 generated in the reaction of cyclopentadienylidene with pyridine in Freon 113



Scheme 2

equilibrated carbene. As k_{pyr} for singlet carbenes is typically $(1-5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, one can estimate τ of CP to be 0.2–1 ns in this solvent.¹⁸ The results of double reciprocal treatments of data generated in several solvents are given in Table 1. Based on product studies^{7,8} and theory (see below), the τ values are likely those of unrelaxed singlet CP.

Table 1. Estimated lifetimes of cyclopentadienylidene in various solvents obtained by standard double reciprocal analysis of the yield of pyridine ylide [assuming $k_{\text{pyr}} = (1-5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$]

Solvent	τ (ns)
Tetrahydrofuran	0.04–0.2
Acetonitrile	0.06–0.3
Pentane	0.1–0.5
Freon-113	0.2–1.0

As seen in Figure 3, cyclopentadienylidene reacts completely with pyridine in Freon 113 when $[\text{pyridine}] \geq 2.5 \text{ M}$. However, Ay is reduced upon LFP of DCP in the presence of a competitive carbene quencher (Q, Scheme 2) such as ethyl acetate (EA). A Stern–Volmer plot of A_y^0/A_y vs $[\text{EA}]$ at constant pyridine concentration (3.3 M) in Freon-113 is linear (Figure 5) with a slope of $k_{\text{EA}}/k_{\text{pyr}}[\text{pyridine}]$, where Ay is the yield of ylide in the presence of quencher. Quenching studies of this type were also performed with methanol and propan-2-ol (Table 2).

The use of pyridine as the ylide-forming reagent is less desirable for the more acidic alcohols (2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoropropan-2-ol) because of the possibility of protonation of pyridine by these alcohols. This problem was avoided by using EA as the ylide-forming reagent. LFP of DCP in neat EA will generate ^1CP , which we expect to be completely captured by solvent to form ylide 8 (Scheme 3). The yield of ylide 8 produced upon LFP of DCP in EA is reduced in the presence of alcohols and other quenchers. Stern–Volmer treatment of the data as before yields $k_{\text{ROH}}/k_{\text{EA}}[\text{EA}]$ or $k_{\text{O}}/k_{\text{EA}}[\text{EA}]$. The results are given in Table 2. Consistent rates of decay of the ylide in the presence of increasing

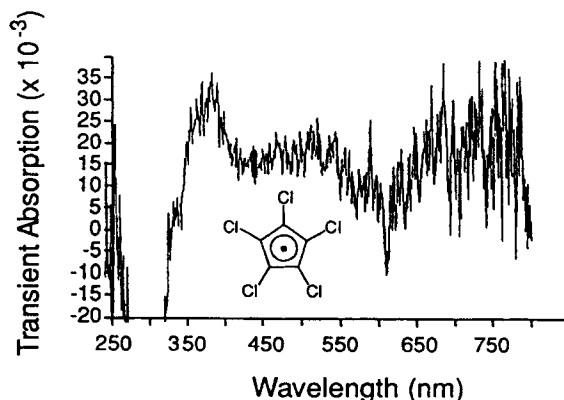


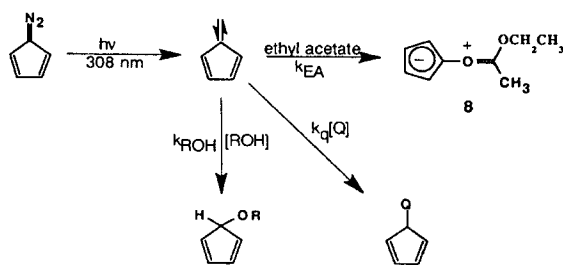
Figure 5. Stern–Volmer quenching of ylide 7 with ethyl acetate in Freon 113

Table 2. Relative rate constants obtained from Stern–Volmer quenching for the reaction of cyclopentadienylidene with various quenchers

Quencher	k_q/k_{DVT}^a	k_q/k_{EA}^b
Methanol	1.4	3.4
Methanol- d_1	1.1 ($k_H/k_D = 1.3 \pm 0.1$)	—
Propan-2-ol	1.0	2.5
2,2,2-Trifluoroethanol	—	5.0
1,1,1,3,3,3-Hexafluoropropan-2-ol	—	8.8
1,1,1,3,3,3-Hexafluoropropan-2-ol- d_1	—	—
Ethyl acetate (EA)	0.48	—
Tetrahydrofuran	—	0.73
Acetonitrile	—	0.56
Freon-113	—	0.23
Pentane	—	0.48

^a Stern–Volmer quenching of the pyridine ylide of cyclopentadienylidene at constant [pyridine] = 3.3 M with Freon 113 as solvent.

^b Stern–Volmer quenching of the ethyl acetate ylide of cyclopentadienylidene **8** in neat ethyl acetate.



Scheme 3

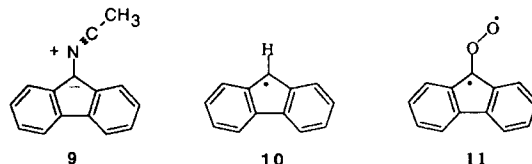
concentrations of alcohol showed that quenching of the yield of ylide resulted entirely from reaction of the alcohol with the carbene and not by attack of the alcohols on the ylides. Acetic acid was not used as a quencher owing to its rapid reaction with the ylides, as evidenced by the increased rates of decay of these ylides.

Fluorenylidene

As noted in previous studies,^{12,13} LFP (XeCl excimer, 308 nm, or XeF excimer, 351 nm) of diazofluorene (DAF) in deaerated acetonitrile produces ¹Fl, which relaxes to ³Fl in less than 1 ns. The triplet carbene has an absorption maximum at 470 nm and is believed to be in rapid equilibrium with a low-lying singlet state. This state is approximately 1 kcal mol⁻¹ higher in energy than the triplet ground state. Spin-equilibrated Fl has a lifetime of 17 ns in acetonitrile and forms a mixture of ylide **9** (major, $\lambda_{\text{max}} = 400$ nm) and fluorenyl radical ¹⁰ (minor, $\lambda_{\text{max}} = 500$ nm).

The fluorenone *O*-oxide **11**, from trapping of the triplet carbene by triplet oxygen, has previously been

studied by LFP and was found to have an absorption maximum at 450 nm.¹⁴



The yield of ylide **9** produced upon LFP of diazofluorene in acetonitrile is reduced in the presence of alcohols and other quenchers. Stern–Volmer treatment of the data as before, but assuming rapid singlet–triplet equilibration, yields $k_{\text{ROH}}/k_{\text{MeCN}}[\text{MeCN}]$ or $k_Q/k_{\text{MeCN}}[\text{MeCN}]$. The results are given in Table 3.

As we have noted, Fl has been studied previously by LFP of DAF and rate constants have been measured for the reaction of Fl with methanol, ethanol and propan-2-ol (8.6×10^8 , 7.3×10^8 and 5.2×10^8 M⁻¹ s⁻¹, respectively).¹³ These numbers differ somewhat from those obtained for Fl with methanol, ethanol and propan-2-ol (5.4×10^8 , 4.7×10^8 and 3.3×10^8 M⁻¹ s⁻¹, respectively) in this study. However, the relative reactivities of these alcohols is the same (methanol 1.6, ethanol 1.4, propan-2-ol 1.0) as determined by both groups. This indicates that the differences between our measurements and those of Schuster and co-workers¹³ are systematic in origin and that the relative reactivities of the alcohols are readily reproducible.

Tetrachlorocyclopentadienylidene

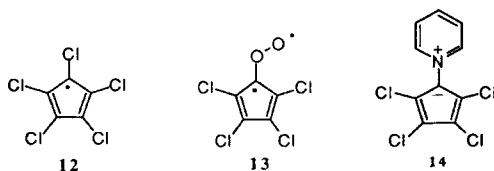
Unlike DCP, LFP (XeCl excimer, 308 nm) of tetrachlorodiazocyclopentadiene (ClDCP) in a freon-type solvent (trichlorofluoromethane) produces a transient spectrum in the UV–visible region with an absorption

Table 3. Rate constants obtained from Stern–Volmer quenching for the reaction of fluorenylidene with various quenchers

Quencher	k_q/k_{MeCN}^a	$k_q \text{ (M}^{-1} \text{s}^{-1})^b \text{ (}\times 10^8\text{)}$
Propan-2-ol	106	3.3
Ethanol	150	4.7
Methanol	175	5.4
Methanol-OD	161	$5.0 \text{ (}k_H/k_D = 1.1 \pm 0.1\text{)}$
2,2,2-Trifluoroethanol	337	10.5
1,1,1,3,3,3-Hexafluoropropan-2-ol	160	5.0
1,1,1,3,3,3-Hexafluoropropan-2-ol- <i>d</i>	161	$5.0 \text{ (}k_H/k_D = 1.0 \pm 0.1\text{)}$
Pyridine <i>N</i> -oxide	157	4.9
Tetramethylurea	62	1.9
Pyridine	52	1.6
THF	30	0.94
Acetonitrile		0.031^b

^a Stern–Volmer quenching of formation of the acetonitrile ylide of fluorenylidene in neat acetonitrile.^b Calculated using $k_{\text{MeCN}} = 3.1 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$ from Ref. 5.

centered at 390 nm (Figure 6). This transient is most likely the pentachlorocyclopentadienyl radical **12** resulting from chlorine abstraction from the solvent by the triplet carbene as its lifetime of several microseconds is too long to be that of the carbene. This reaction has considerable precedent. Fluorenylidene is



known^{12,13} to abstract chlorine atoms readily from chlorocarbons. This was confirmed by LFP (308 nm) of hexachlorocyclopentadiene in Freon 113, which also

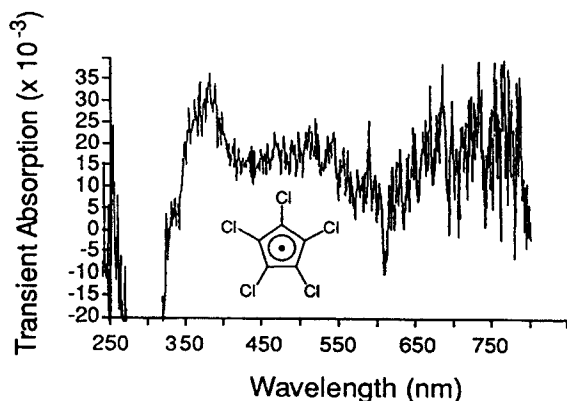


Figure 6. Transient absorption spectrum of **12** produced by LFP of tetrachlorodiazocyclopentadiene in Freon 113. The spectrum was recorded 500 ns after a 308 nm laser pulse over a window of 500 ns

afforded a 390 nm transient. The lifetime of this transient in both cases is on the scale of tens of microseconds and appears to be controlled by the concentration of precursor and the initial yield of transient, as expected for a free radical.

When oxygen is bubbled through a solution of tetrachlorodiazocyclopentadiene for 2–3 min prior to irradiation, the 390 nm peak is replaced with a broad absorption band centered at *ca* 380 nm (Figure 7, Scheme 4). The position and profile of the transient are in reasonable agreement with those of tetrachlorocyclopentadienone *O*-oxide (**13**, $\lambda_{\text{max}} = 420 \text{ nm}$) observed in matrix studies at low temperature.¹⁶

LFP of tetrachlorodiazocyclopentadiene in the presence of pyridine in Freon-113 produces ylide **14** (Figure 8, Scheme 5). The yield of ylide **14** grows with increase in pyridine concentration until 0.2 M pyridine, after which it remains constant. In the case of ClCP,

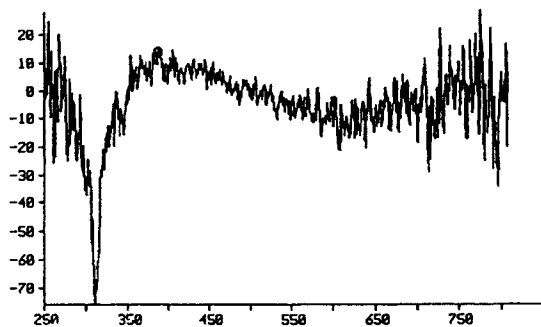


Figure 7. Transient absorption spectrum of **13** produced by LFP of tetrachlorodiazocyclopentadiene in Freon 113. The sample was aerated by bubbling oxygen through the solution for 3 min prior to irradiation. The spectrum was recorded 500 ns after a 308 nm laser pulse over a window of 500 ns

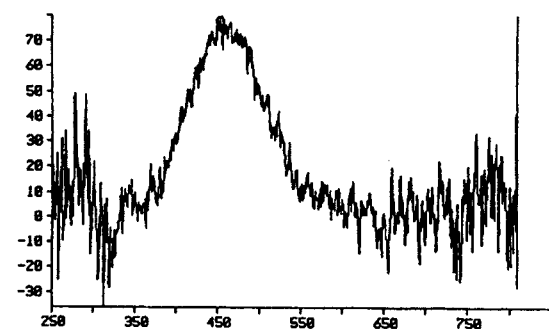
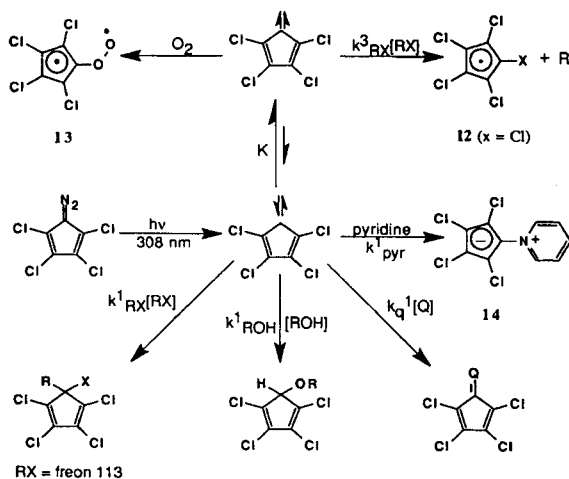


Figure 8. Transient absorption spectrum of **14** produced by LFP of tetrachlorodiazocyclopentadiene in the presence of pyridine with Freon 113 as the solvent. The spectrum was recorded 500 ns after a 308 nm laser pulse over a window of 500 ns

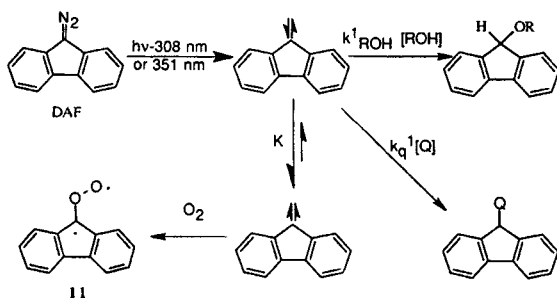


Table 4. Rate constants obtained from Stern–Volmer quenching for the reaction of tetrachlorocyclopentadienylidene with various quenchers

Quencher	$k_{\text{ROH}}/k_{\text{pyr}}^a$	k_q^b ($\text{M}^{-1} \text{s}^{-1}$) ($\times 10^8$)
Propan-2-ol	0.72	7.2
Ethanol	0.65	6.5
Methanol	0.41	4.1
Tetramethylurea	1.3	13
Tetrahydrofuran	0.73	7.3

^a Stern–Volmer quenching of the pyridine ylide of tetrachlorocyclopentadienylidene at constant [pyridine] = 1.65 M with Freon 113 as an inert solvent.

^b Assuming $k_{\text{pyr}} = 1 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$.

the triplet is assumed to interconvert rapidly with the singlet on the basis of chemical trapping studies reported in the literature.¹¹ This results in the equation $k_{\text{pyr}}/k_{\text{RX}}[\text{RX}] = k_{\text{pyr}}\tau$, which assumes that there is no significant reaction of $^3\text{ClCP}$ with solvent (small $^3k_{\text{RX}}$) in the presence of saturating concentrations of pyridine.

The yield of pyridine ylide at constant pyridine concentration (1.65 M) was reduced in the presence of methanol, propan-2-ol, tetrahydrofuran and tetramethylurea. Stern–Volmer treatment of the data affects the information in Table 4.

Owing to the lack of detectable non-pyridine ylides of $^1\text{ClCP}$, rate constants for quenching of this carbene could not be measured accurately for more acidic alcohols.

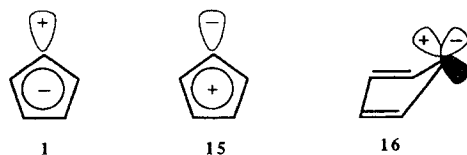
DISCUSSION

Cyclopentadienylidene and fluorenylidene

The three carbenes studied exhibit an interesting mix of behaviors. The triplet state is the ground state of cyclopentadienylidene (CP), yet it cannot be detected chemically in solution or spectroscopically by trapping with oxygen. On the other hand, both $^3\text{ClCP}$ and ^3Fl indeed are formed in solution as demonstrated, by their ability to react with oxygen to form carbonyl ylides. In this respect, our LFP studies are consistent with previous product studies performed at room temperature.^{7,8} This indicates that ^1CP is either much more reactive and shorter lived than $^1\text{ClCP}$ or ^1Fl and/or that intersystem crossing in this carbene is particularly inefficient.

Salem and Rowland¹⁹ have predicted that closed shell singlet carbenes will undergo spin–orbit-assisted intersystem crossing (ISC) to triplet carbenes more rapidly than open-shell singlet carbenes. Theory¹⁰ predicts that the lowest energy singlet state of ^1CP is planar and open shell and does not resemble closed shell configurations such as **1** or **15**. If theory is correct, then this explains the failure of ^1CP to relax rapidly to ^3CP in solution, prior to reaction with solvent. Theory¹⁰

predicts that the lowest energy closed-shell singlet of CP is non-planar (e.g. **16**), thus ISC to the triplet will again be slow because closed-shell singlet CP and planar ^3CP will have different geometries, in which case this radiationless transition will have a poor Frank-Condon factor.



The sign of the slope of the Brønsted plots for CP and FI demonstrates an increasing reaction rate of the carbene with increasing OH bond polarity/acidity of the alcohol ($\text{p}K_{\text{a}}$ data of Ballinger and Long²⁰). This appears to indicate that the H atom of the OH bond is actively involved in the transition states of the reactions. The small magnitude of the slopes, however, reflects a very small degree of charge development in the transition state. These observations are consistent with either direct insertion or protonation with a very early transition state, but do not appear to be consistent with ylide formation as the dominant reaction mechanism.

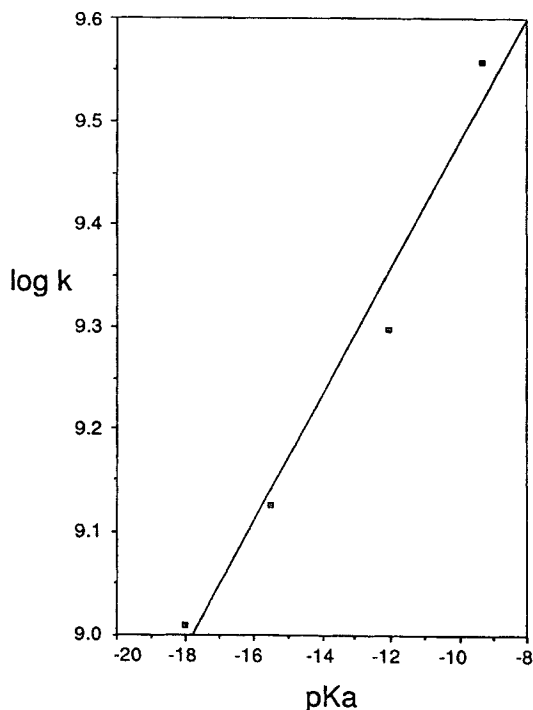


Figure 9. Brønsted plot for the reaction of CP with various alcohols

CP and FI react faster with alcohols than with ethers or esters, which should be better ylide-forming reagents than alcohols.

The relative reactivities of CP and FI with alcohols is in contrast with the behavior expected if these carbenes had large contributions from a resonance structure such as **1**. Again we note that recent calculations have indicated that neither structure **1** nor structure **15** are energy minima.¹⁰ Instead, the lowest energy singlet of CP is planar and open shell and the lowest energy closed shell singlet is the non-planar variant **16** of electron configuration **15**. The calculations indicate that there is little delocalization between the carbene center and the butadiene portion of the molecule in **16**.¹⁰ The highly reactive singlet chemistry of CP, the low yield of triplet and the reactivity patterns towards alcohols and ethers are not inconsistent with the closed-shell singlet structure **16**, a highly reactive and unstabilized carbene which should exhibit reactivity patterns similar to that of methylene.²¹⁻²³ However, the data with methylene have been interpreted in favor of an ylide type mechanism in the gas phase and in solution.²¹⁻²³

Our data are easily reconciled with a concerted insertion reaction of closed-shell singlet **16** with alcohols in which there is a small amount of polarization of the H—O bond in the transition state (**17**).

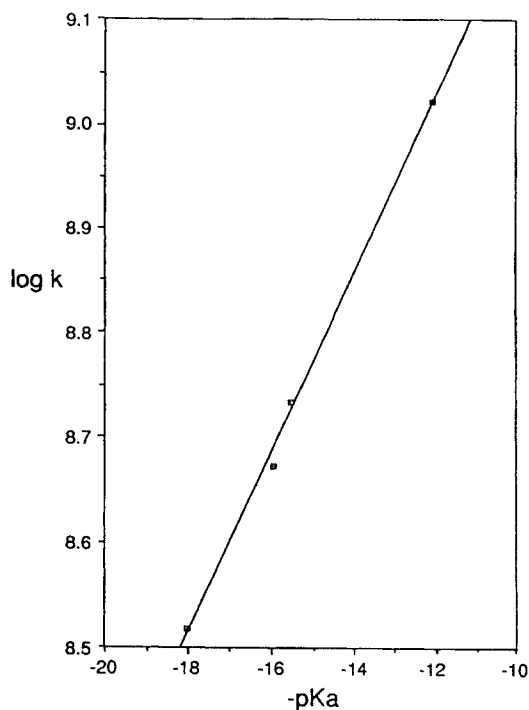
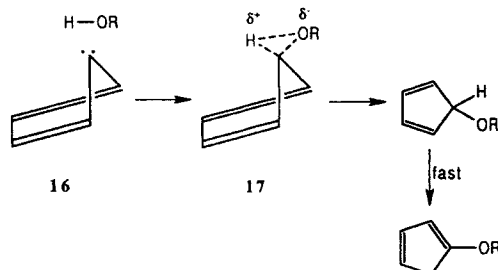
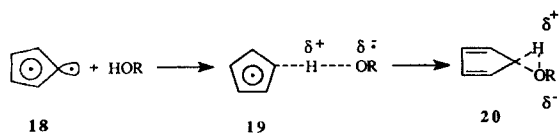


Figure 10. Brønsted plot for the reaction of FI with various alcohols.



However, the data with CP are also consistent with a planar biradical such as singlet **18**, the lowest energy singlet state calculated by theory.¹⁰ One can explain the relative reactivity of ¹CP with alcohols as being due to a slightly polarized hydrogen atom transfer (transition state **19**) which leads to planar, triangular structure **20** followed by concerted insertion reaction.



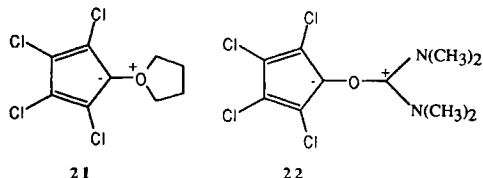
These mechanisms are essentially the concerted OH insertion process pictured earlier accompanied by a small amount of charge separation. This interpretation explains why increasing acidity of the alcohol increases the reaction rate and why CP reacts faster with alcohols than with ethers, which certainly react by the slower ylide mechanism under our conditions. It is possible that the direct insertion mechanism is faster than the ylide mechanism because there may be a contribution of quantum mechanical tunneling to the motion of the small, light migrating hydrogen atom in the former mechanism.

We believe that a concerted OH insertion reaction of ¹Fl with alcohols is also the best interpretation of our data, although earlier workers have decided in favor of the ylide mechanism.²¹⁻²³ Like ¹Cp, ¹Fl is most reactive towards more acidic alcohols and reacts faster with alcohols than with ethers. We are reluctant to conclude, however, that ¹Fl is an open-shell singlet biradical or is locked into a non-planar structure, as predicted for ¹CP, however, because ¹Fl and ³Fl rapidly interconvert.^{12,13} It is possible that the open- and closed-shell forms of planar ¹Fl are very close in energy. Alternatively, if ¹Fl is indeed closed shell and non-planar, this form must be close in energy to the planar geometry.

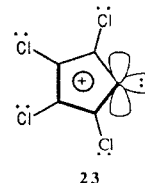
The mechanism proposed is a direct insertion reaction with a transition state which has only a slight charge separation. The reaction product should isomerize extremely rapidly, because alkoxy cyclopentadienes have never been isolated and the isomerization of 5-methylcyclopentadiene is far more rapid than the isomerization of its 1- and 2-substituted isomers.

Tetrachlorocyclopentadienylide (ClCP)

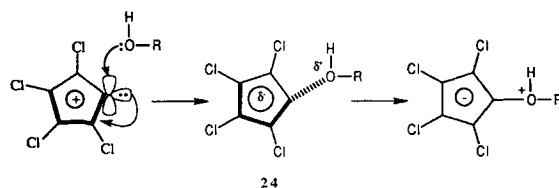
The data with ClCP favor the expected ylide mechanism (Table 4). The absolute reactivity of ClCP no longer tracks the acidity of the alcohol. Furthermore, tetrahydrofuran and tetramethylurea, which are expected to form particularly stable ylides **21** and **22**, respectively, and which cannot undergo proton transfer reactions, react with ClCP more rapidly than do the alcohols.



We speculate that the four chlorine substituents stabilize the planar closed-shell singlet configuration **23** by π electron backbonding, which brings the energy of this configuration below that of the open shell singlet.



This allows rapid ISC to the triplet carbene. Furthermore, it allows access of an aromatic transition state in the reaction with alcohols in which the alcohol oxygen lone pair attacks the carbene from above the plane of the five-membered ring, in concert with electron flow from the doubly occupied sigma orbital into the π system, to form transition state **24**. This speculation invites high level *ab initio* calculations of the lowest energy singlet state of ClCP.



CONCLUSION

Our LFP studies further reinforce the elusive nature of triplet CP at room temperature, while triplet ClCP and triplet Fl are readily trappable by oxygen. Significant differences were observed in the reactivity of alcohols with ClCP versus CP and Fl. The increasing reactivity of alcohols with decreasing acidity and the greater reactivity of Lewis bases such as THF and pyridine clearly indicate an ylide mechanism for the reaction of

alcohols with ClCP. On the other hand, alcohols and especially more acidic alcohols are more reactive than common ylide formers, such as pyridine and THF? with CP and FI. The slopes of Brønsted plots indicate that there is only slight positive charge development on the alcohol proton in the rate-determining step. These results point to protonation with a very early transition state or more likely a concerted OH insertion reaction of alcohols with CP and FI with a small amount of charge separation in the transition state. The greater reactivity of more acidic alcohols with a number of highly reactive carbenes (methylene,²¹⁻²³ cyclopentadienylidene fluorenylidene and phenylcarbene²⁴) is indicative of a protonation or direct insertion mechanism. However, product studies appear to contradict these conclusions by supporting an ylide mechanism of reaction of alcohols with methylene,²¹⁻²³ fluorenylidene¹³ and possibly cyclopentadienylidene.¹⁵ It is possible that a mixture of mechanisms operates, as suggested for 2-(hydroxymethyl)phenylcarbene.⁶ It seems likely that all three mechanisms of reaction proceed rapidly with very short-lived singlet carbenes such as CP, FI and methylene, and the operative reaction path may vary with the experimental conditions.

EXPERIMENTAL

Materials. Solvents were purified and dried by distillation from calcium hydride.

Diazocyclopentadiene (DCP). Diazocyclopentadiene was prepared and purified by literature procedures.²⁵ Because of its highly explosive nature, distillation was performed under reduced pressure with heating not exceeding 60°C. The resulting solid was dissolved in Freon-113 and stored in a freezer.

Diazofluorene.²⁶ 'Activated' manganese dioxide²⁷ (3 g) was added to a solution of fluorenone hydrazone (2 g) in dry chloroform (30 ml) and stirred for 24 h, at which time TLC showed complete conversion to product. After removal of manganese dioxide by filtration, subsequent purification was performed as described in the literature.

Tetrachlorodiazocyclopentadiene (ClDCP).²⁸ 'Activated' manganese dioxide²⁷ (3 g) was added to a solution of tetrachlorocyclopentadiene hydrazone¹¹ (1.2 g) in dry chloroform (20 ml) and stirred for 24 h, at which time TLC showed complete conversion to product. After removal of manganese dioxide by filtration, subsequent purification was performed as described in the literature.¹¹

Laser flash photolysis (LFP). The LFP apparatus used has been described previously.²⁹ LFP experiments

were performed with 308 nm laser light generated from a Lambda Physik LPX 100 excimer laser (XeCl). The absorption of all samples used in kinetic studies ranged from 0.4 to 0.9 at 308 nm. Laser samples were deaerated by bubbling nitrogen for 2–3 min. The pyridine and ethyl acetate ylides of cyclopentadienylidene were monitored at wavelengths of 535 and 440 nm, respectively, the acetonitrile ylide of fluorenylidene 400 nm and the pyridine ylide of tetrachlorocyclopentadienylidene at 450 nm. All experiments were performed at ambient temperature.

Transient spectra. Transient spectra were recorded 500 ns after a 308 nm wavelength laser pulse over a window of 500 ns using an EG&G Princeton Applied Research Model 1460 optical multi-channel analyser.

Double-reciprocal lifetime studies. Samples were prepared using a stock solution of diazo precursor (100 µl), varying the amounts of pyridine and enough of the particular solvent of interest to bring the total volume to 1.5 ml.

Stern–Volmer kinetic studies. For the determination of rate constants using the pyridine ylide, runs were performed using multiple samples with constant concentrations of diazo precursor and pyridine (2.5 M for diazocyclopentadiene and 0.2 M for tetrachlorocyclopentadiene). Various amounts of quencher were used with Freon-113 added to give a constant total volume (2 ml). For the determination of rate constants using the ethyl acetate or acetonitrile ylides, ethyl acetate or acetonitrile was used as solvent and added quencher did not exceed 10% by volume (200 µl) of the total solution (2 ml). All Stern–Volmer studies of CP and ClCP were performed with 308 nm laser radiation. Stern–Volmer studies of FI used 308 nm or 351 nm laser radiation. No wavelength dependence was observed for FI in any of the cases tested.

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Table 5. pK_a s of the alcohols used as quenchers¹⁹

Alcohol	pK_a
Propan-2-ol	18.0
Ethanol	15.9
Methanol	15.5
2,2,2-Trifluoroethanol	12.0
1,1,1,3,3,3-Hexafluoropropan-2-ol	9.3

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